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# Mass-Spectrometric Study of the Rhenium-Oxygen System

Rhenium, having the second-highest melting point (3180°C) among metals, invites many applications for use both for refractory containers used in high-temperature studies, and in technologies. Its growing utilization for high-temperature applications has generated immediate need for knowledge of the thermodynamic properties of its compounds. Thus the thermodynamic values for rhenium oxide systems have been determined by mass spectrometry and x-ray diffraction. The experimental procedure, resultant data, and other results are reported (see ref.).

Three solid oxides of rhenium are well established: the dirhenium heptoxide ( $Re_2O_7$ ), the trioxide ( $ReO_3$ ), and the dioxide ( $ReO_2$ ). The thermodynamic properties of  $Re_2O_7(s)$  have been well established from low-temperature heat capacity, bomb calorimetry, and vapor-pressure measurements, whereas the properties of  $ReO_2(s)$  and  $ReO_3(s)$  are incomplete or uncertain. In particular the low-temperature heat capacities of  $ReO_2(s)$  and  $ReO_3(s)$  have not been measured, and the results of vapor-pressure studies have shown considerable disagreement.

The purpose of this investigation was to examine in detail the equilibrium vapors over thermodynamically defined systems. The vaporization behaviors of the two-phase solid systems (Re + ReO<sub>2</sub>) and (ReO<sub>3</sub>) were studied by means of the Knudsen effusion method and mass-spectrometric observations, followed by x-ray-diffraction identification of the residual phase after cooling of the material to room temperature.

The vapor phase in equilibrium with each of the two systems is the same, primarily  $Re_2O_7(g)$  with only a minor amount (<5%) of  $ReO_3(g)$ . The condensed phases were identified before and after vaporization by x-ray-diffraction analysis. Mass-spectrometric

data were combined with the mass-loss effusion data to yield the following equations for the vapor pressure (calculated as Re<sub>2</sub>O<sub>7</sub>):

For reaction  $3\text{ReO}_3(s) = \text{ReO}_2(s) + \text{Re}_2\text{O}_7(g)$ ,

$$\log P(\text{atm}) = 12.529 \pm 0.270 - [(11,913 + 173) / T]$$

$$(612^{\circ}-710^{\circ}\text{K})$$
 with  $\Delta H_{l}^{\circ} = 54.5 \pm 0.8$  kcal/mole

For reaction 
$$7/2 \text{ ReO}_2(s) \Rightarrow 3/2 \text{ Re}(s) + \text{Re}_2O_7(g)$$
,

$$\log P(\text{atm}) = 14.442 \pm 0.145 - [(20,447 + 143)/T]$$

(961°-1087°K) with 
$$\Delta H_l^{\circ} = 93.5 \pm 0.7$$
 kcal/mole

The thermodynamic properties were recalculated to 298°K by estimation of a constant  $\Delta C_p \approx -4$  cal/deg. mole for the sublimation reactions

$$\Delta H_f$$
° 298 [ReO<sub>2</sub>(s)] = -102.8 ± 2.0 kcal/mole  
 $S$ ° 298 [ReO<sub>2</sub>(s)] = 13.5 ± 1.6 eu  
 $\Delta H_f$ ° 298 [ReO<sub>3</sub>(s)] = -140.7 ± 2.0 kcal/mole  
 $S$ ° 298 [ReO<sub>3</sub>(s)] = 19.3 ± 1.5 eu

In the course of the study, the appearance potential of Re<sub>2</sub>O<sub>7</sub>(g) was found to be  $13.0 \pm 0.5$  eV.

### Reference:

Battles, J. E.; Gundersen, G. E.; Edwards, R. K.: J. Phys. Chem., vol. 72, 1968, p. 3963. Edwards, R. K.: A Mass Spectrometric Study of the Rhenium Oxide System. Argonne National Laboratory, 15 Dec. 1967.

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### Notes:

- 1. This information may interest the metals industry.
- 2. Inquiries concerning this information may be directed to:

Office of Industrial Cooperation Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439 Reference: B69-10645

> Source: J. E. Battles, G. E. Gundersen, and R. K. Edwards Chemical Engineering Division

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Mr. George H. Lee, Chief Chicago Patent Group U.S. Atomic Energy Commission Chicago Operations Office 9800 South Cass Avenue Argonne, Illinois 60439